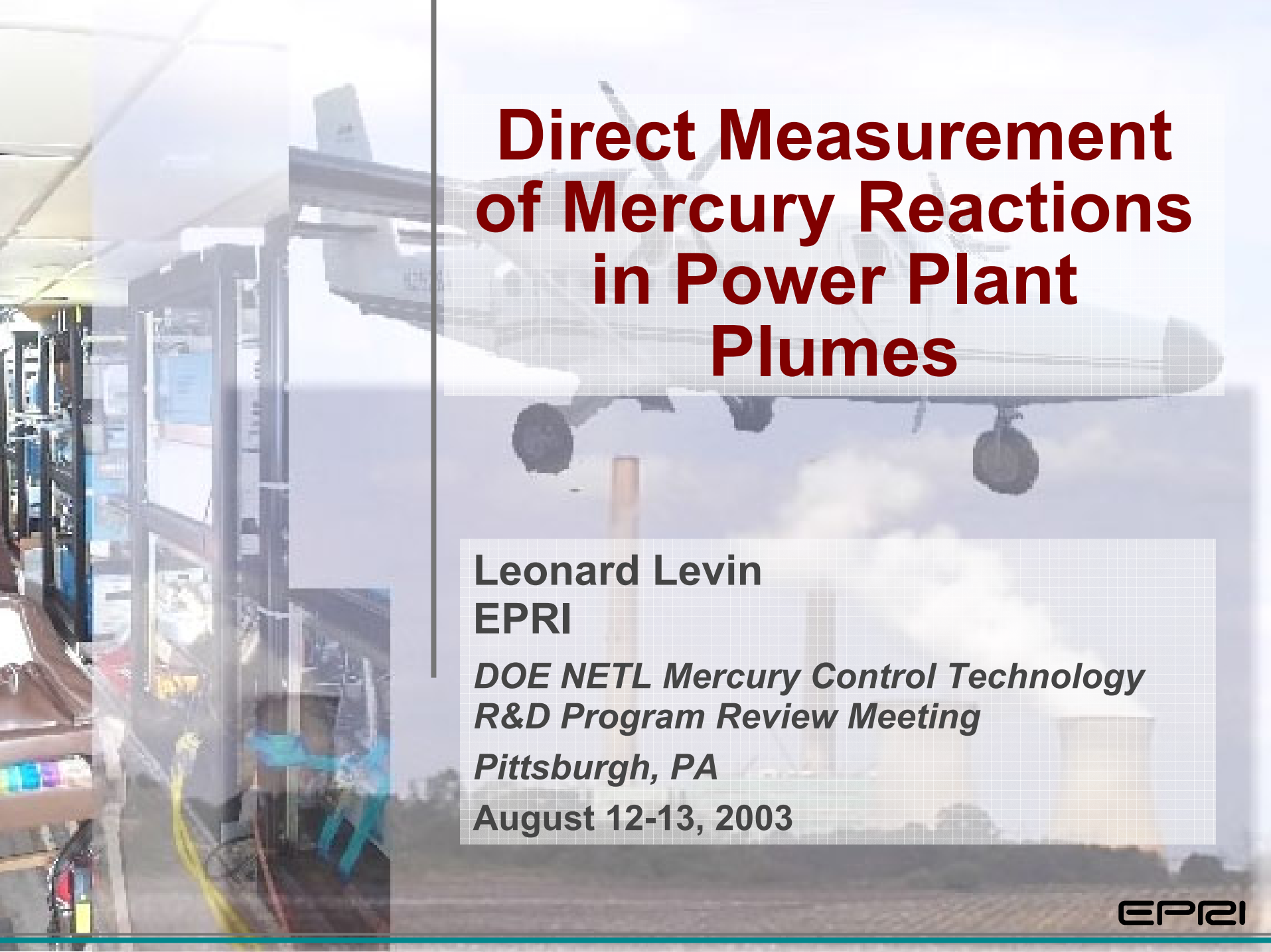


Direct Measurement of Mercury Reactions in Power Plant Plumes

Leonard Levin
EPRI

DOE NETL Mercury Control Technology R&D Program Review Meeting

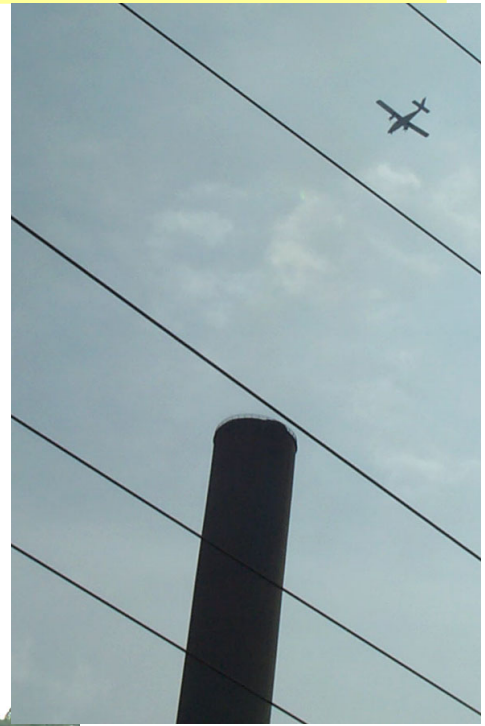
Pittsburgh, PA

August 12-13, 2003

EPRI

Power plant plumes may promote rapid mercury chemistry

- *Ionic* mercury (6 orders of magnitude more water soluble, easily washed out of plume) → rapidly reduced to …
- *Elemental* mercury (much less soluble in precipitation, likely to go into regional, global background) in power plant plumes.



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GENERAL ORDER OF DISCUSSION

- Current modeling of mercury in plumes
- Evidence for plume reactions of mercury
- Experimental plan
- Measurements at Plant Bowen
- Plant Bowen results
- Plans for Pleasant Prairie experiment
- Hint of a mechanism??
- Research team

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CURRENT MODELING OF MERCURY IN PLUMES

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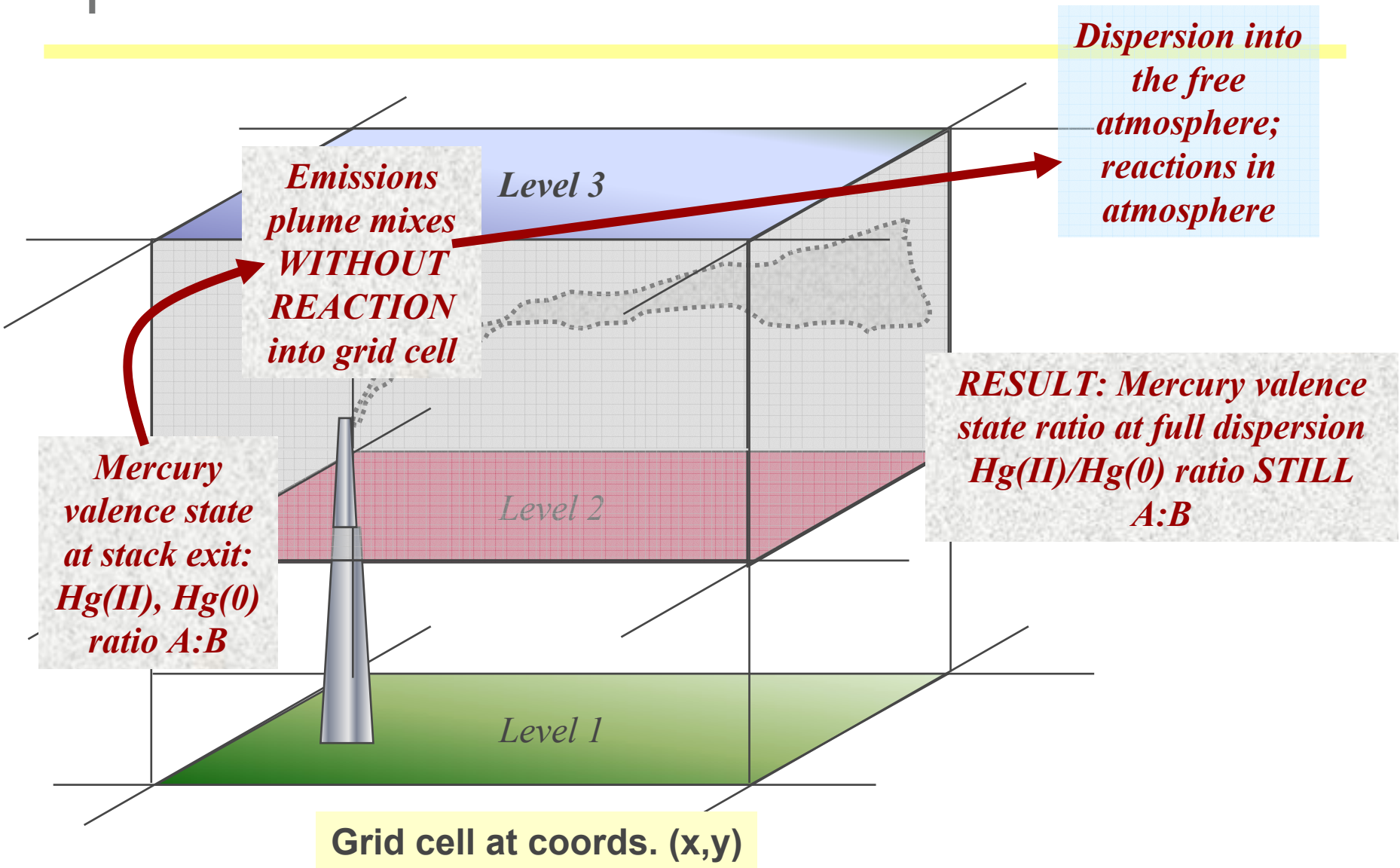
Plume behavior in model atmosphere



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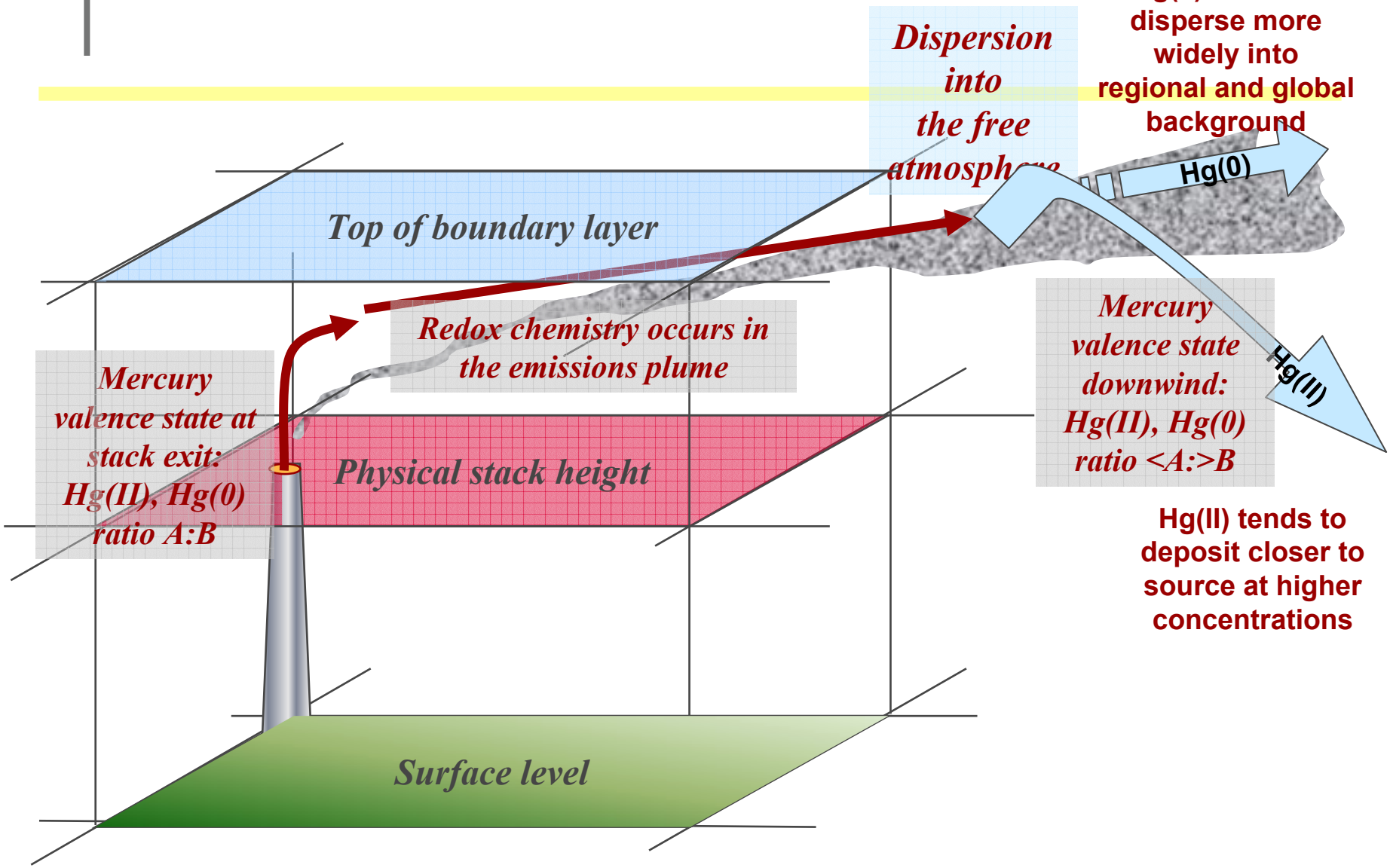
Plume behavior in “real” atmosphere



Hg(0) tends to disperse more widely into regional and global background

Hg(II) tends to deposit closer to source at higher concentrations

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EVIDENCE FOR PLUME REACTIONS OF MERCURY

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– PLUME DILUTION SIMULATIONS

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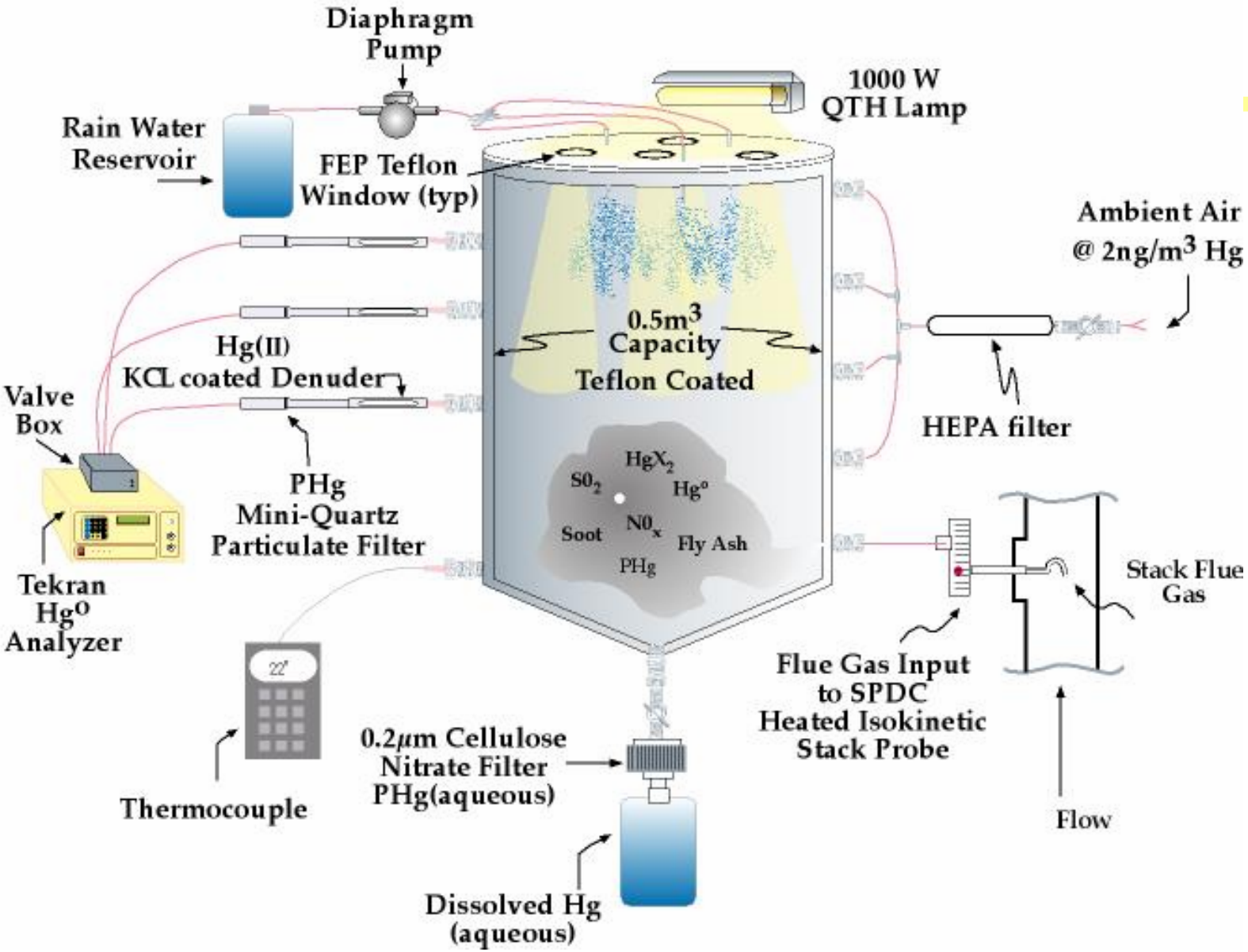
Static Plume Dilution Chamber (SPDC) Schematic



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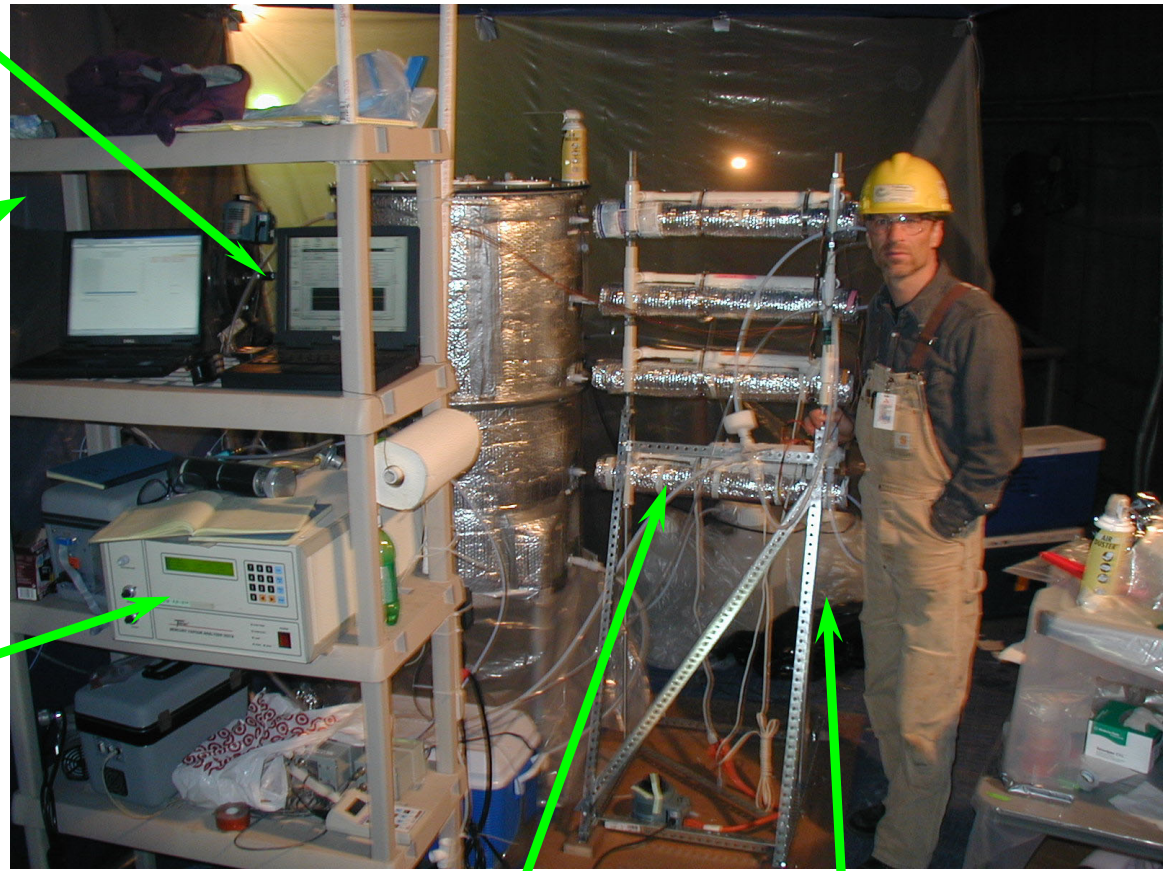
SPDC at Plant Bowen

Duct to SPDC Interface

Flue gas Duct

Tekran Real-Time Hg(0)



SPDC Speciation Denuder/Filter System

Rainwater Wash System

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Some SPDC Study Locations

- October 2002 at Plant Bowen, EPRI (Levin), Southern Company, (Jansen), in collaboration with TVA (Valente) and EERC (Laudal and Schulz)
- March 2000 @ EERC UARG-EPRI (Michaud and Levin), CATM-EERC (Laudal), EPA-ORD (Kilgroe) and FGS (Prestbo)
- May 1997 @ Dickerson and Mont. Co. Waste Inc. Maryland DNR-PPRP (Sherwell) and ERM (J. Ross)
- February 1995 @ WEPCO-PIPP Wisconsin DNR (Knauer) and EPA GLNPO(A. Bandemeier)

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SPDC EERC Pilot Plant Study Conclusions: Hg(II) ➔ Hg(0) in Plume

- $Hg(0)/Hg_{TOT}$ at end > ratio injected into the SPDC – Hg(II)→Hg(0)?
- Conversion is fast (<5 minutes), significant
- Greater conversion of Hg(II) to Hg(0) for SPDC "daytime" runs.
- Conversion of Hg(II) to Hg(0): typically x1.5-3, largest (x6) when O_3 added at 200 ppb.
- No SPDC runs showed significant amounts of gaseous Hg(II) adsorbing to the particulate phase

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– REGIONAL MODEL SIMULATIONS vs. OBSERVATIONAL DATA

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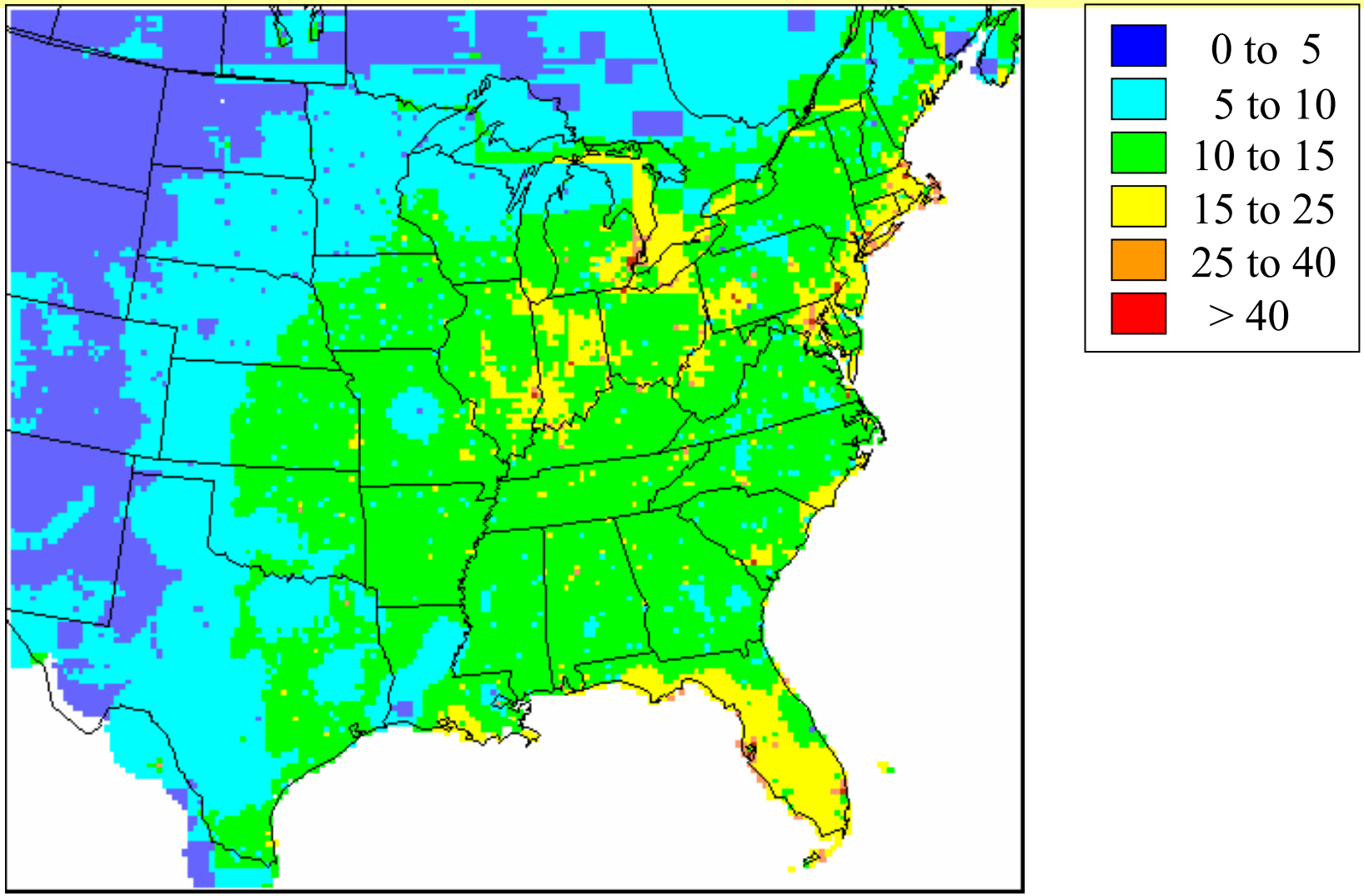
Annual wet deposition flux of total Hg (μg/m^2-y)
(EPRI TEAM Regional Model, 20-km resolution)



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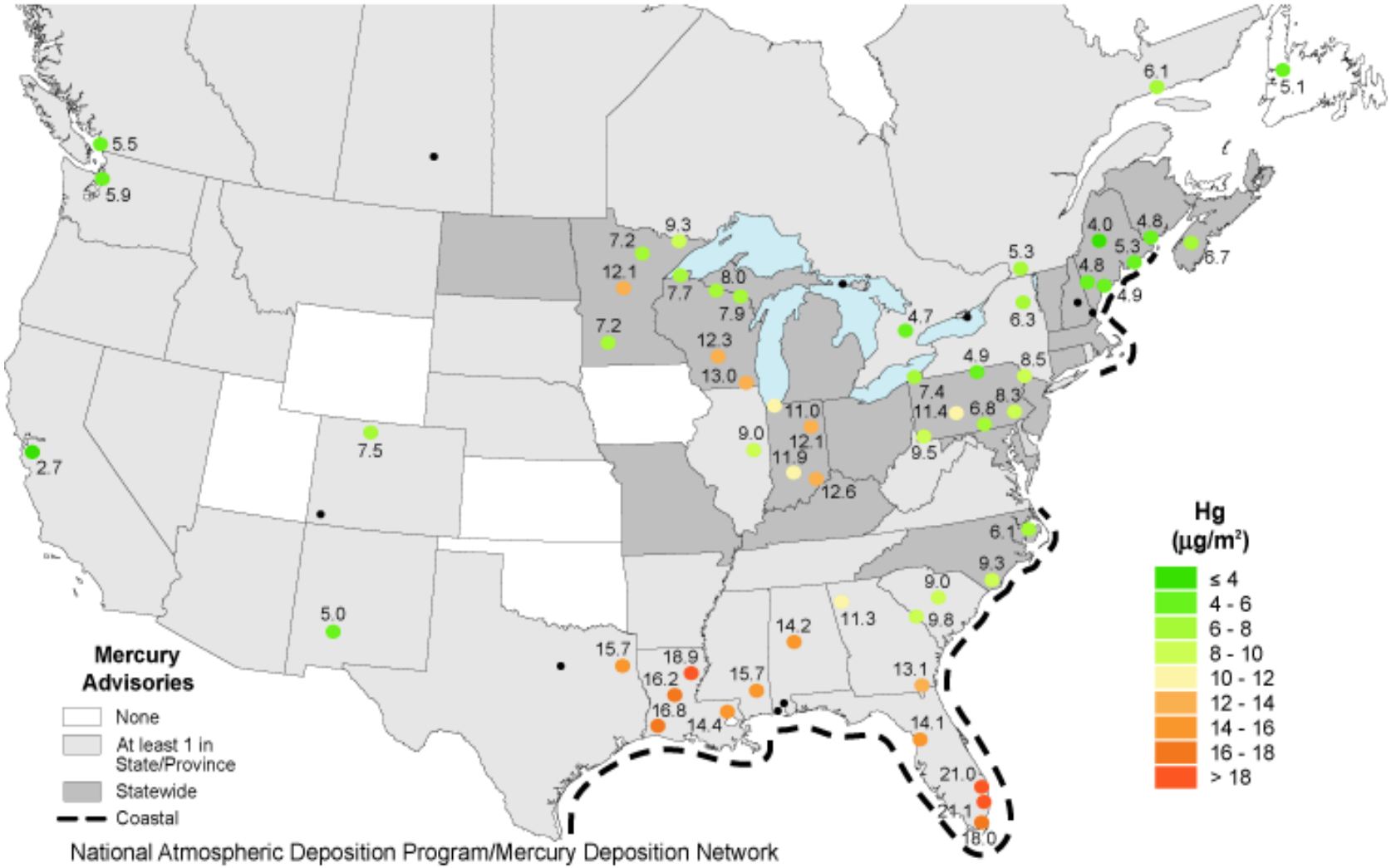
Observed Mercury Wet Deposition (µg/m^2-y), Mercury Deposition Network, 2001



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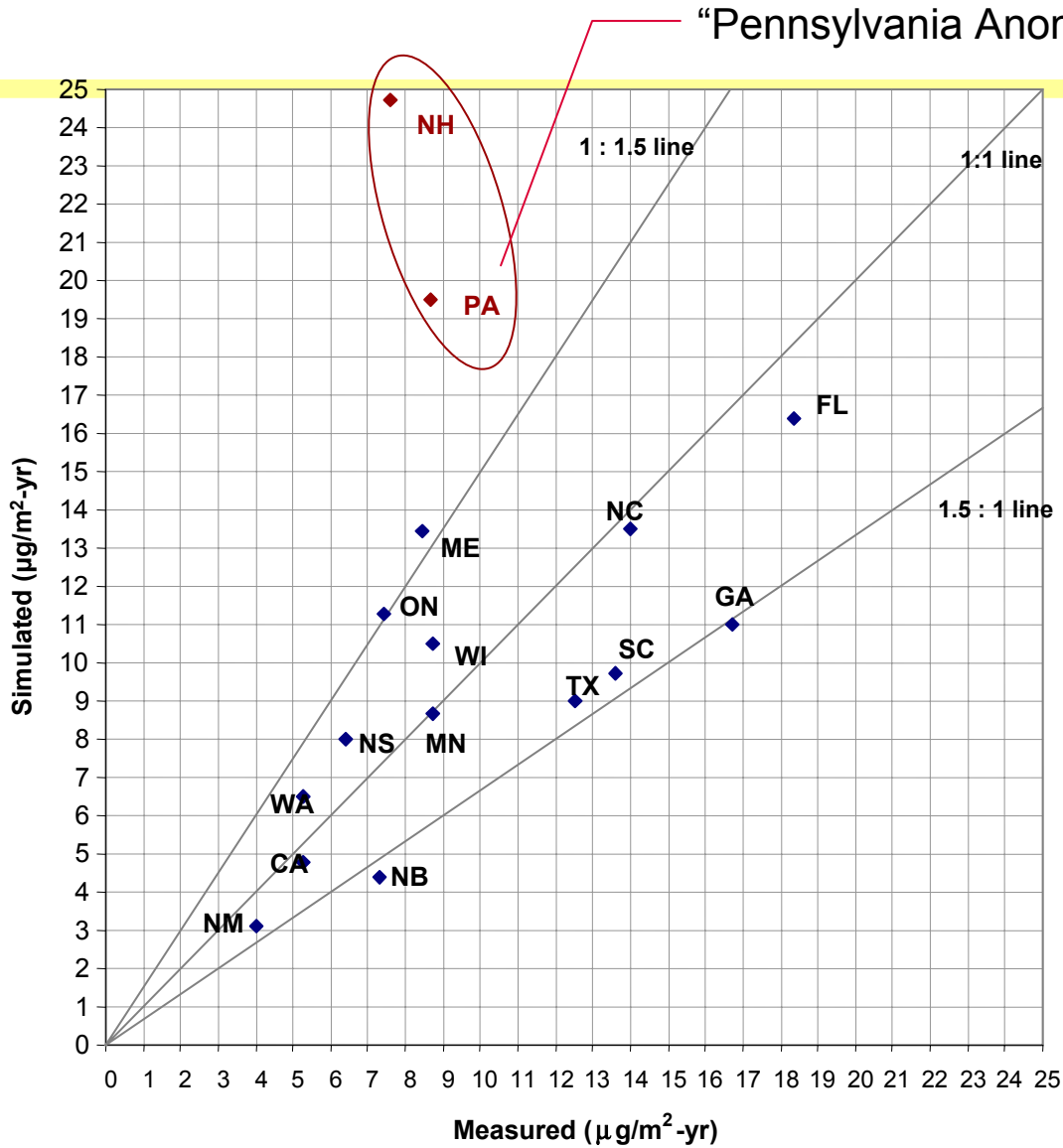
EPRI TEAM Model Prediction vs. Observations
Wet Deposition Data Averaged by State



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– FIELD MEASUREMENTS, SOURCE vs. SAMPLER SPECIATION

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Simulations vs. Measurements, Plant Bowen to Yorkville Ground Station

	Emissions	Ambient measurements	TEAM simulations without clouds	TEAM simulations with clouds [a]
SO_2/NO_y	3.2	3.5	3.1	2.9
SO_2/Hg ($x10^5$)	8.2	6.4	7.8	7.3
$Hg(0)/Hg_{TOT}$	0.40	0.94	0.41	0.42
$Hg(II)/Hg_{TOT}$	0.60	0.06	0.59	0.58

[a] *Clouds placed between 450 m and 2000 m above ground level*

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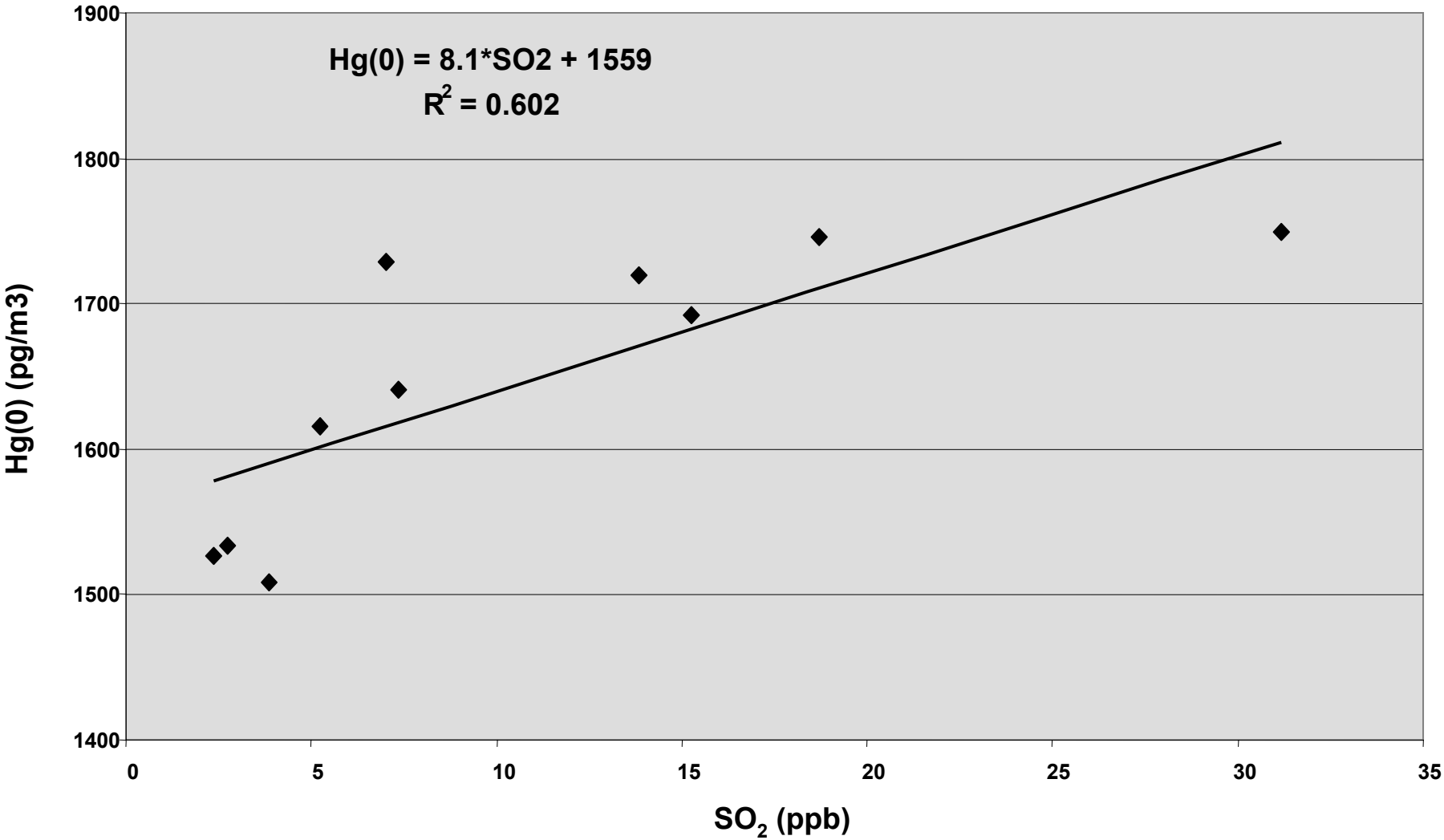
Hg(0) vs. SO_2 – July 20, 2001 Event, Bowen Plume Impingement at Yorkville Station



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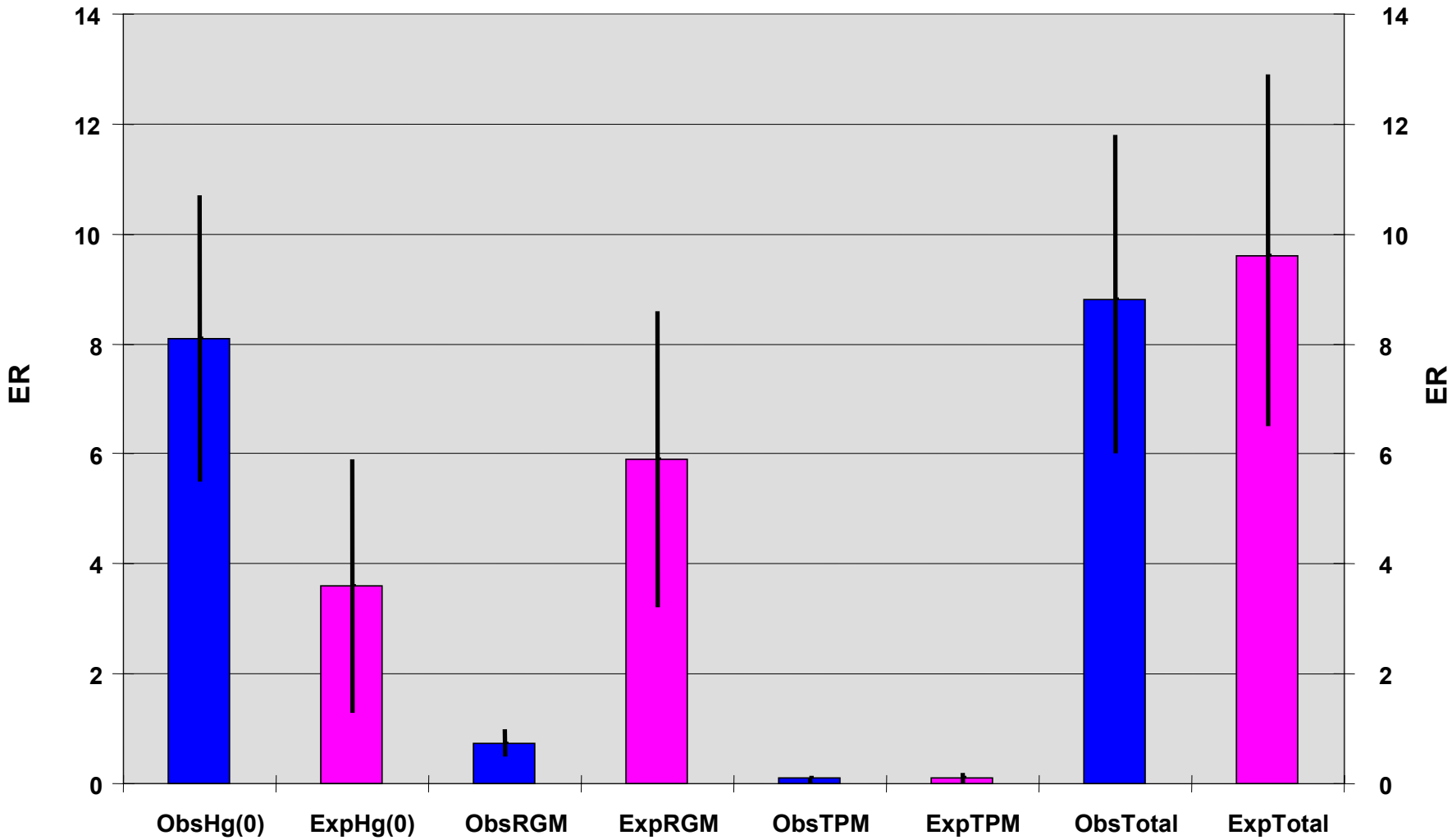
Observed vs. Expected Emission Ratios (pg/m^3 *per* ppb) – July 20, 2001 Event, Bowen Plume Impingement at Yorkville Station



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EXPERIMENTAL PLAN

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WORKING HYPOTHESES

- $Hg(II)/Hg_{TOT}$: [stack gases]>[aircraft]>[ground station]
- From plume dilution experiments: look for rapid, high-ratio chemical reduction in buoyancy segment of plume out to dilution ratio of hundreds to one.
- Ideally:
  - Steady, unidirectional winds < 15 m/s; low turbulence BL
  - Aircraft sampling of upwind background (free of other major sources), several downwind transects (each with multiple passes), far downwind dispersion
  - Aircraft multiple passes through plume rise portion just above stack
- Reality: a lot more difficult (approach to stack; steady-state conditions;
- Additional goal: method evaluation, plume dilution methods

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MEASUREMENTS AT PLANT BOWEN

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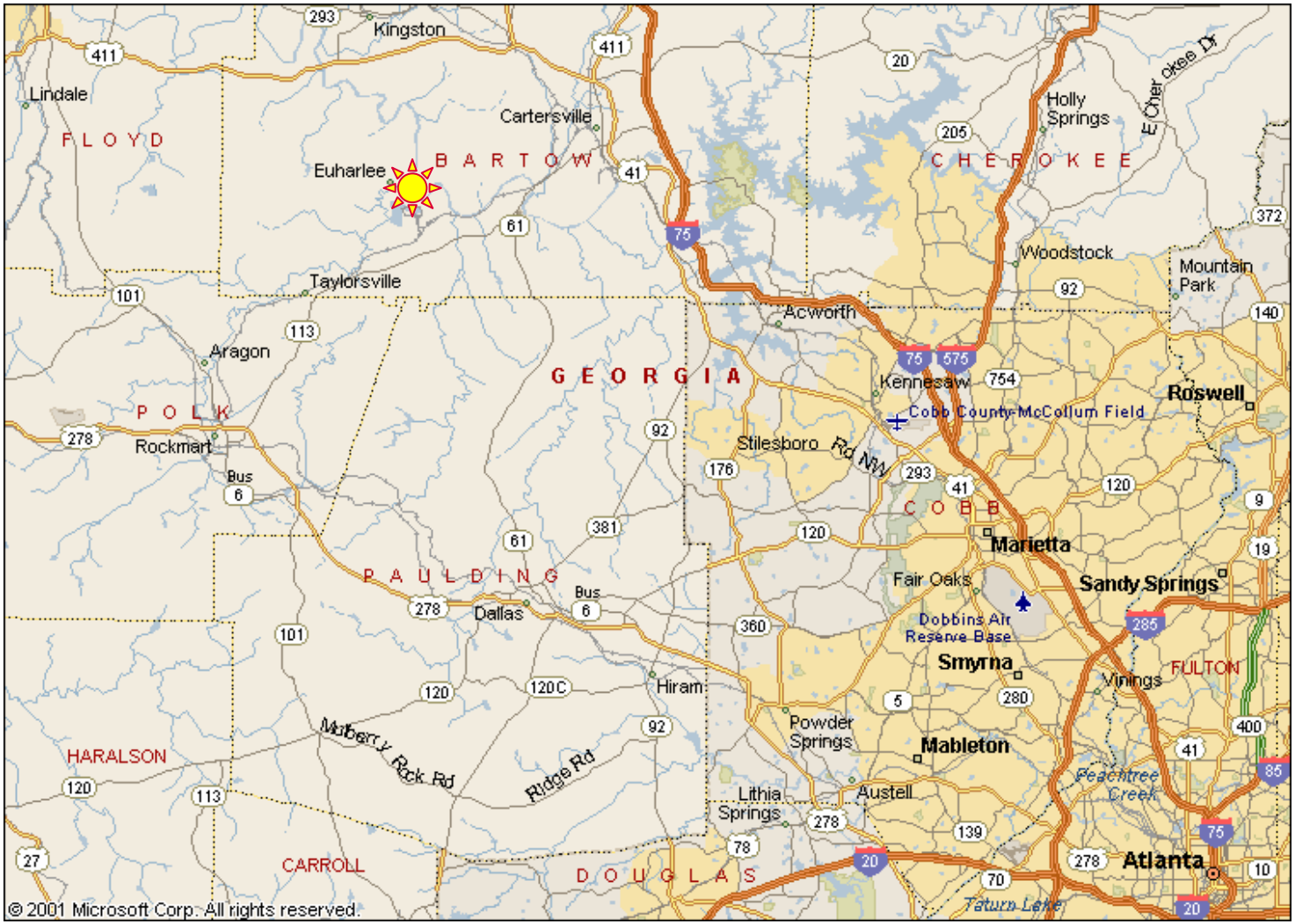
Plant Bowen, Georgia Power



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Plant Bowen

- Located NW of Atlanta, gently rolling terrain, plateau to SSW (location of ground station)
- Twin stacks, 300+ m ht, each venting 2 units through single duct within RC structure
- Units 1, 2, 4 operating; Unit 1 had operating SCR
- Coordinated measurements: stack OH, stack SPDC Tekran, aircraft Tekrans, ground supersite Tekrans

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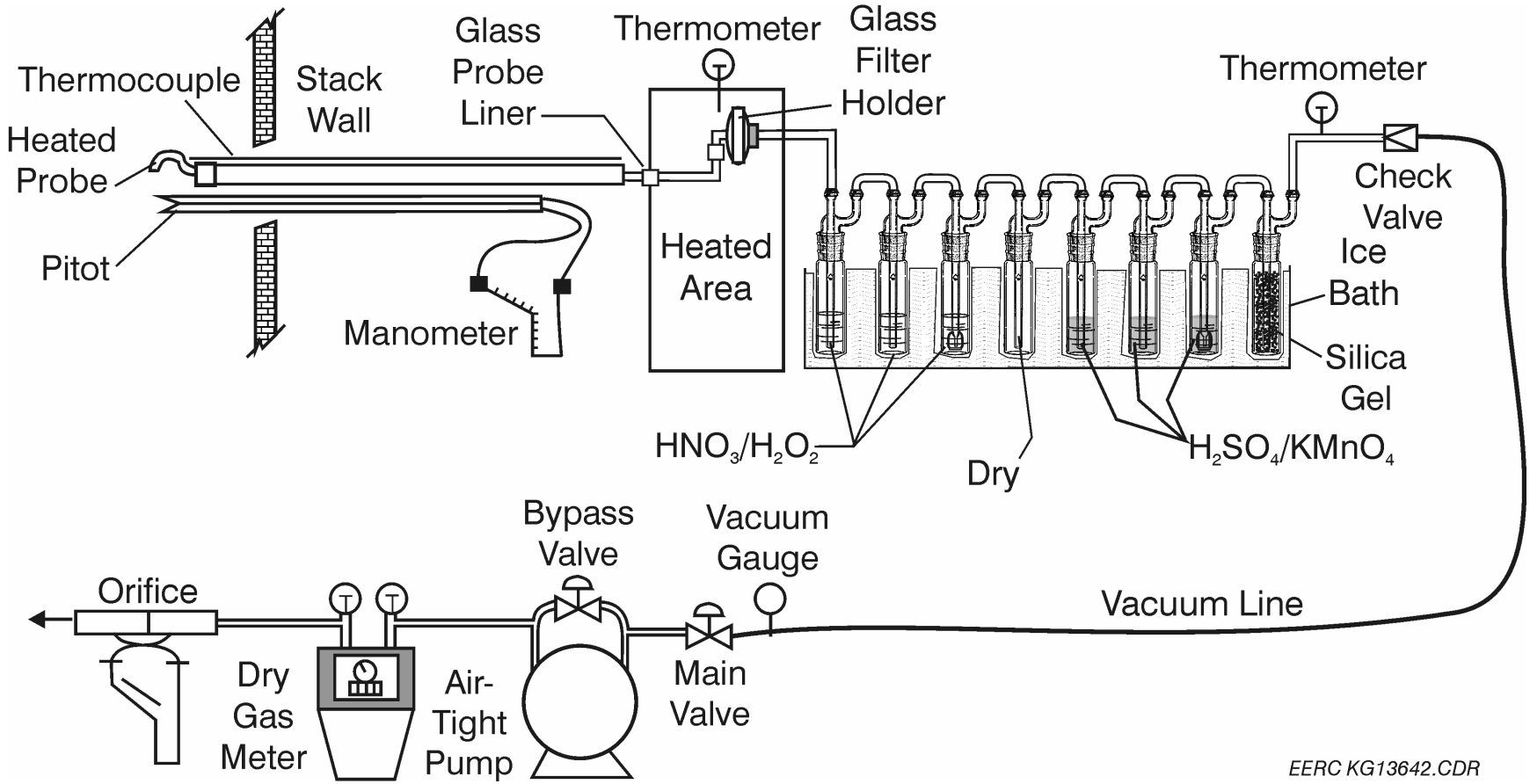
Ontario Hydro Method



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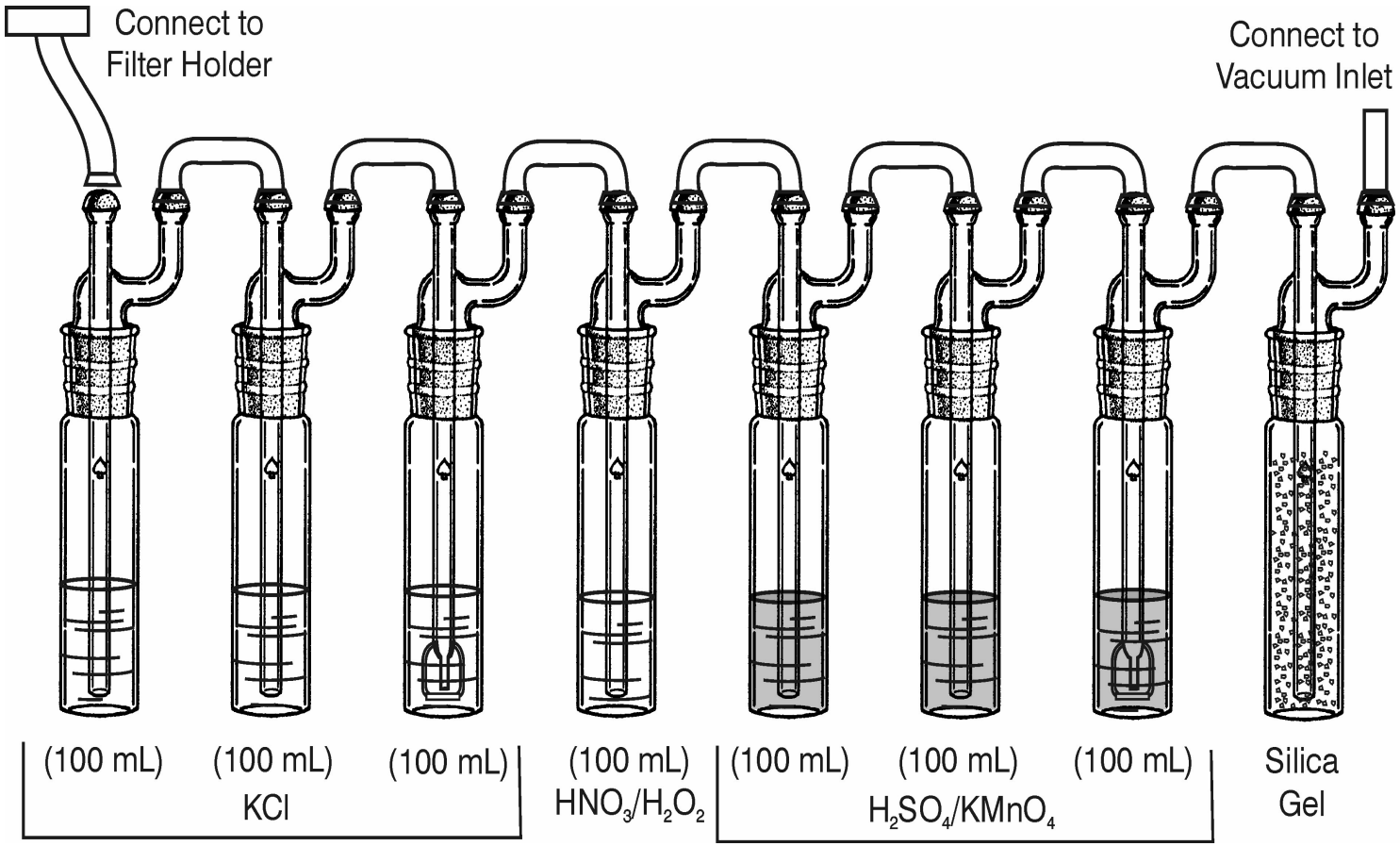
Sample Train, Ontario Hydro Method



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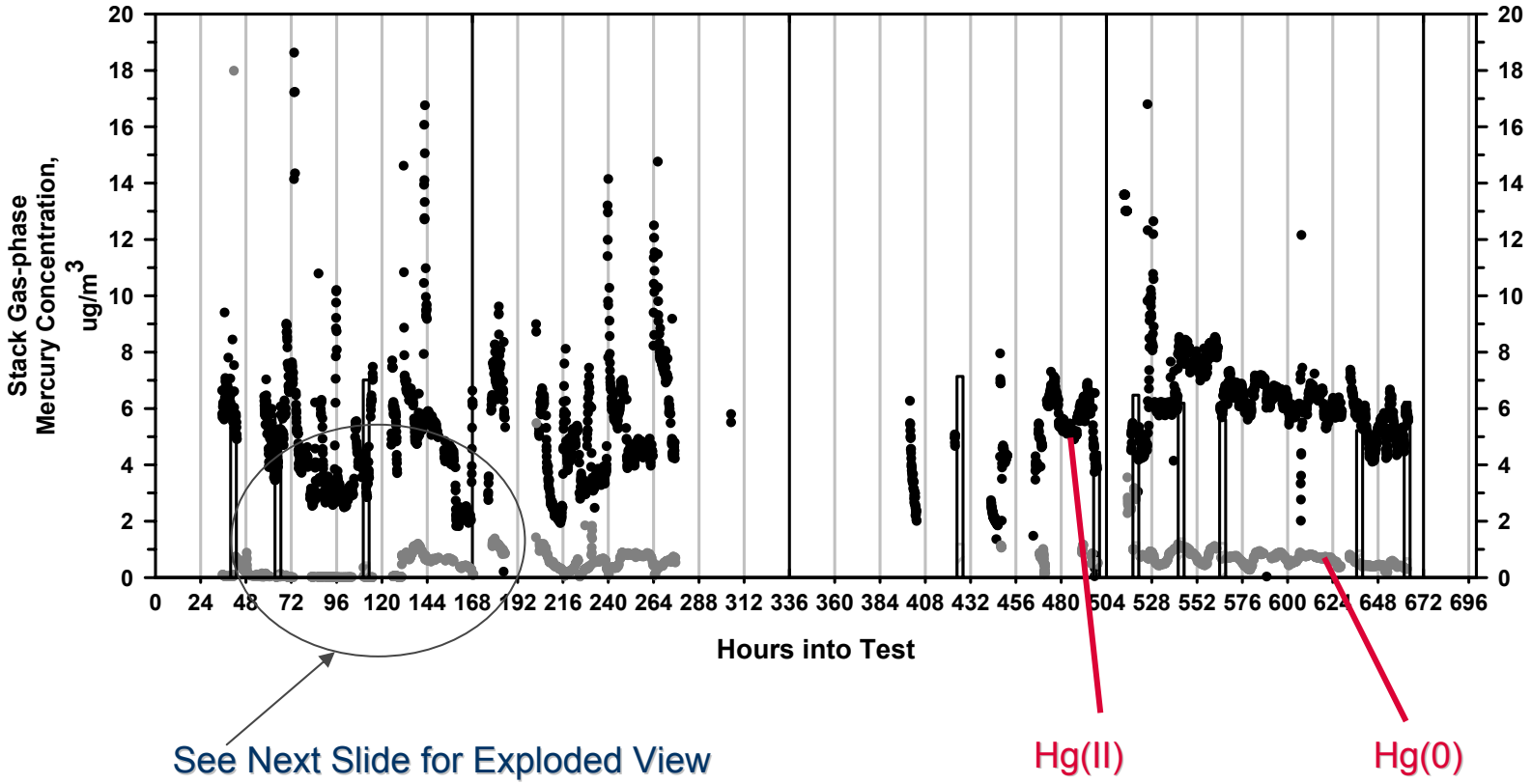
Bowen Unit 2 Stack Data



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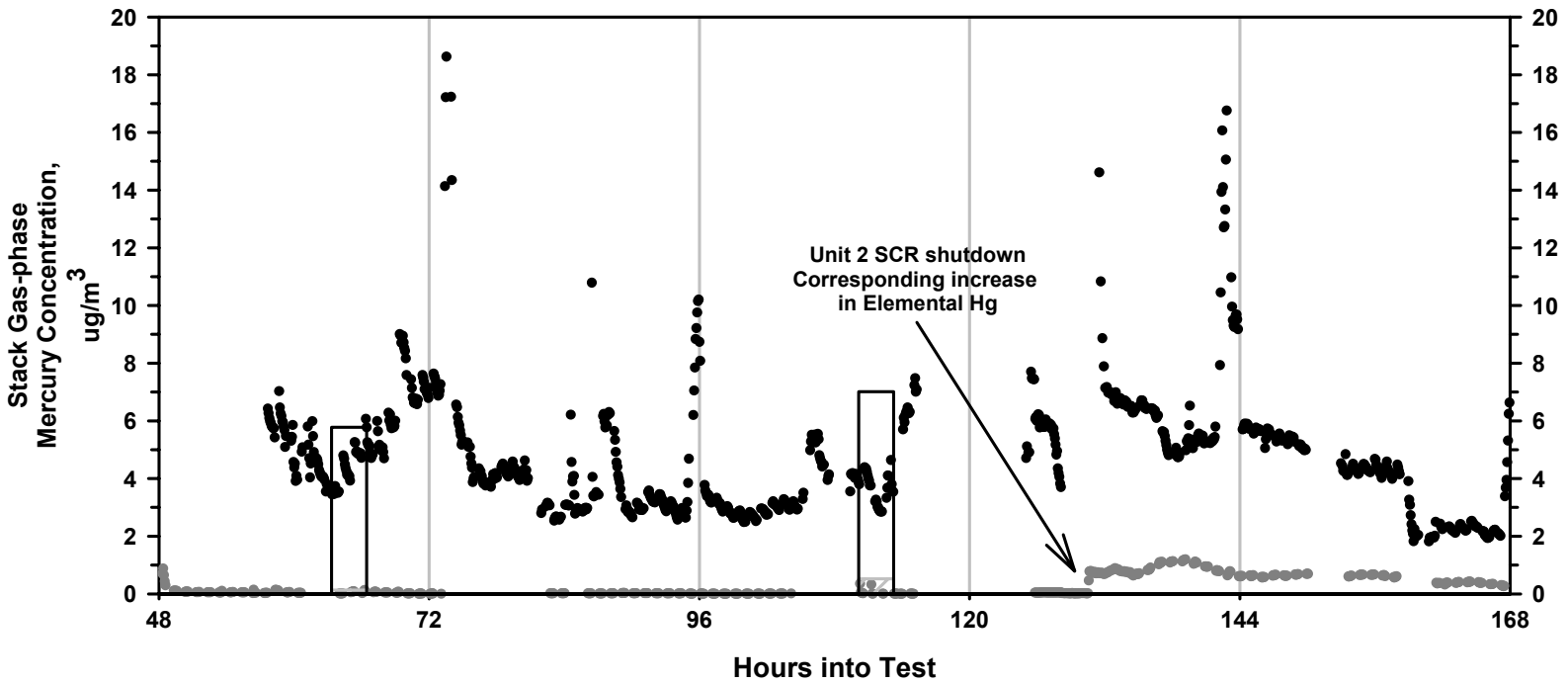
Bowen Unit 2 Stack CMM Data



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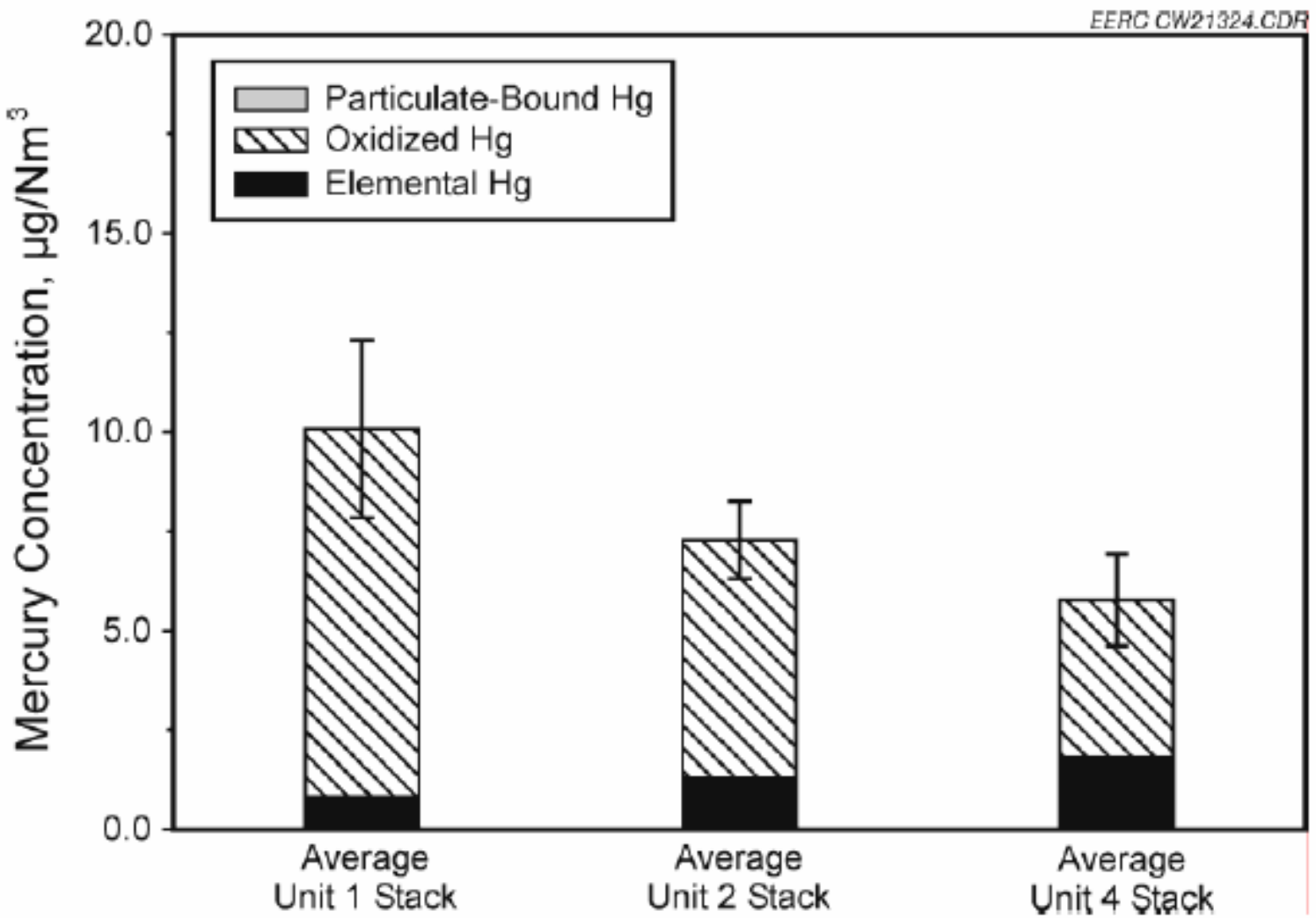
Plant Bowen Stack Data



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Aircraft Plume Sampling

- Annular denuders used to capture RGM
- Hg(0) captured by the Tekran gold trap
- Particulate-bound mercury is captured by a filter, then desorbed to the analyzer
- Plume eddy/boundary detection using a NOx analyzer

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Twin Otter International
DHC-6-300 Vistaliner

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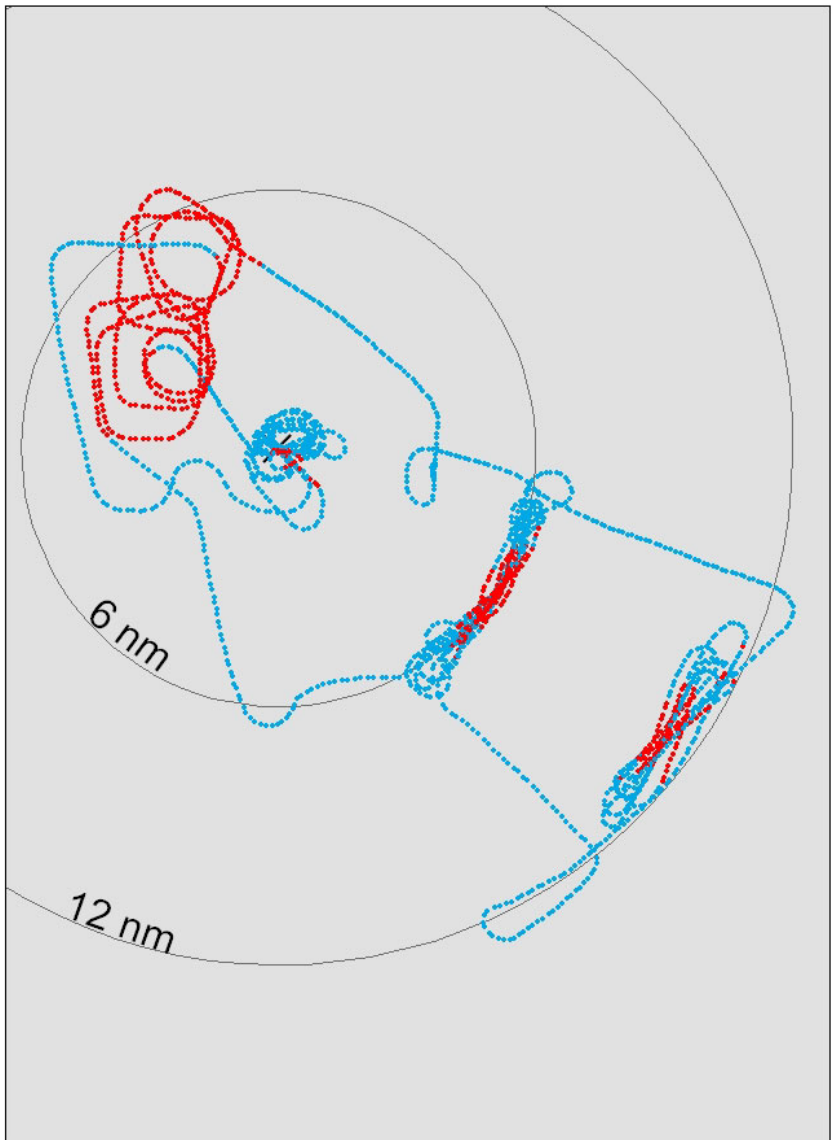
Typical Bowen Flight Track



Flight 6
October 17, 2002
1245h-1541h
(segments in red denote Tekran capture of ambient samples)

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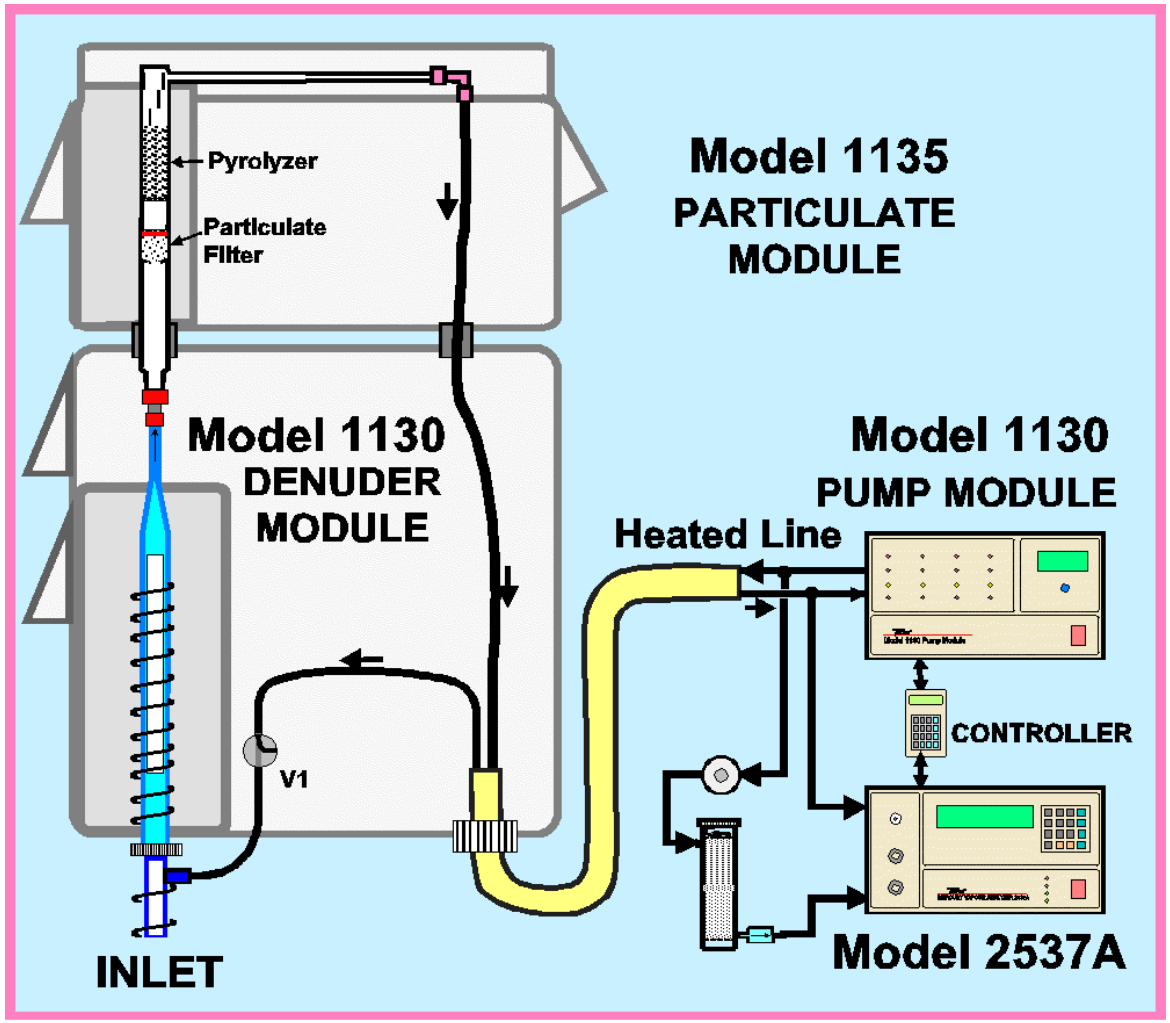
Tekran Automated Hg Analyzer



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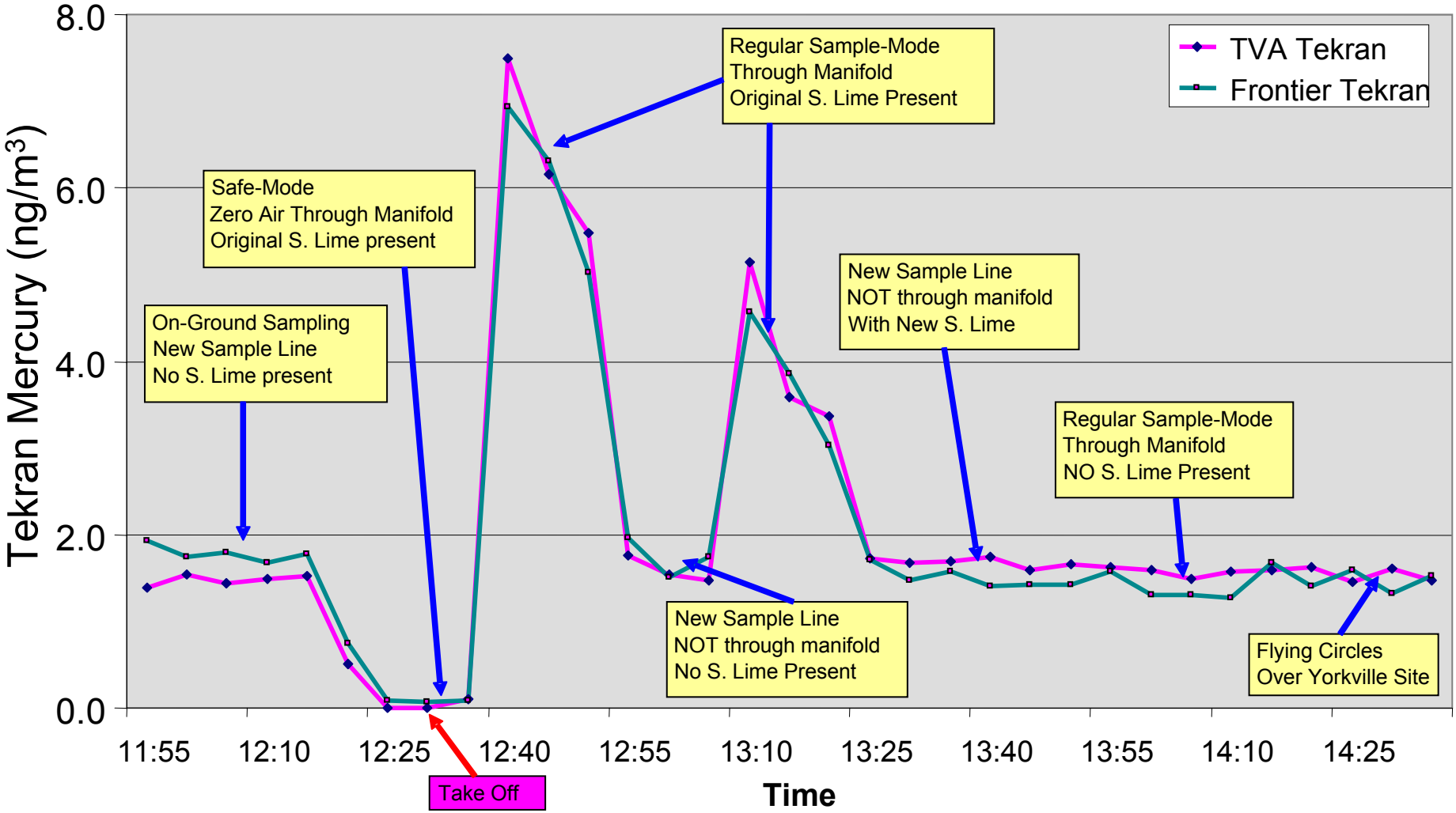
Tekran Intercomparison During Aircraft Sampling



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RGM and particle mercury concentrations (pg/m^3) for 4 Bowen sampling flights

Flight Number		0 nm	6 nm	12 nm
2	Dilution Factor	2103	3629	16443
	RGM	1206	616	152
	Particle	n.d.	n.d.	25
4	Dilution Factor	654	11436	24545
	RGM	407	359	296
	Particle	33	12	8
6	Dilution Factor	219	11273	11340
	RGM	9054	327	299
	Particle	1177	5	4
7	Dilution Factor	407	6614	9072
	RGM	5663	648	374
	Particle	43	13	11

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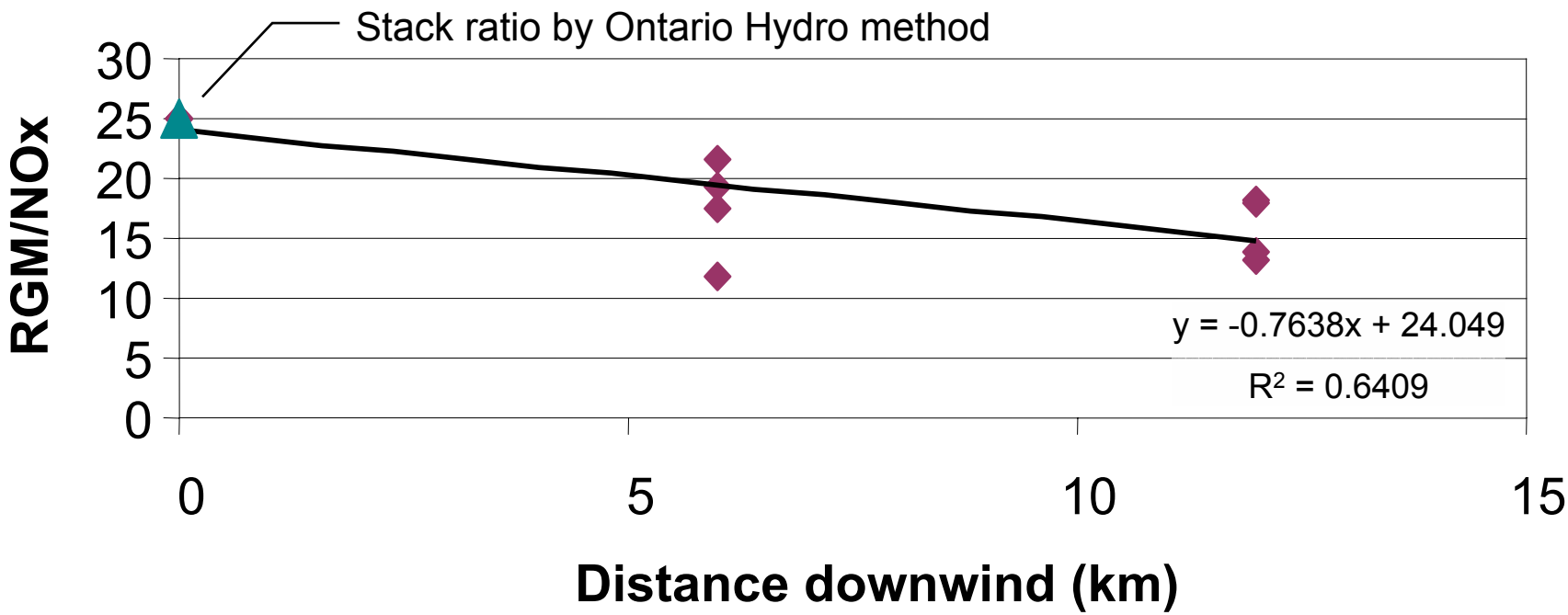
RGM/NOx vs Downwind Distance, 4 Sampling Flights



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PLANS FOR PLEASANT PRAIRIE EXPERIMENT

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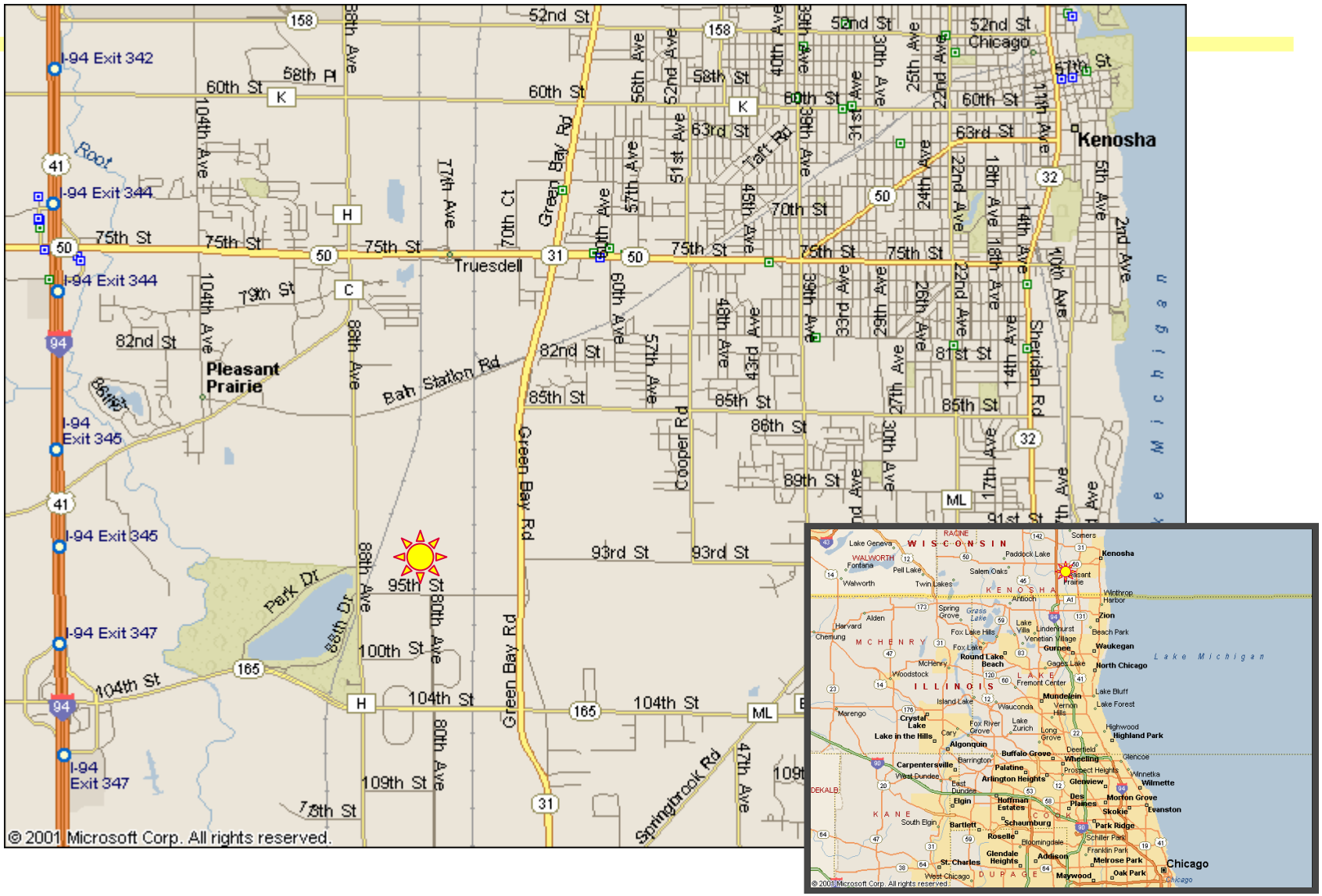
Pleasant Prairie Power Plant, We Energies



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Pleasant Prairie Plant

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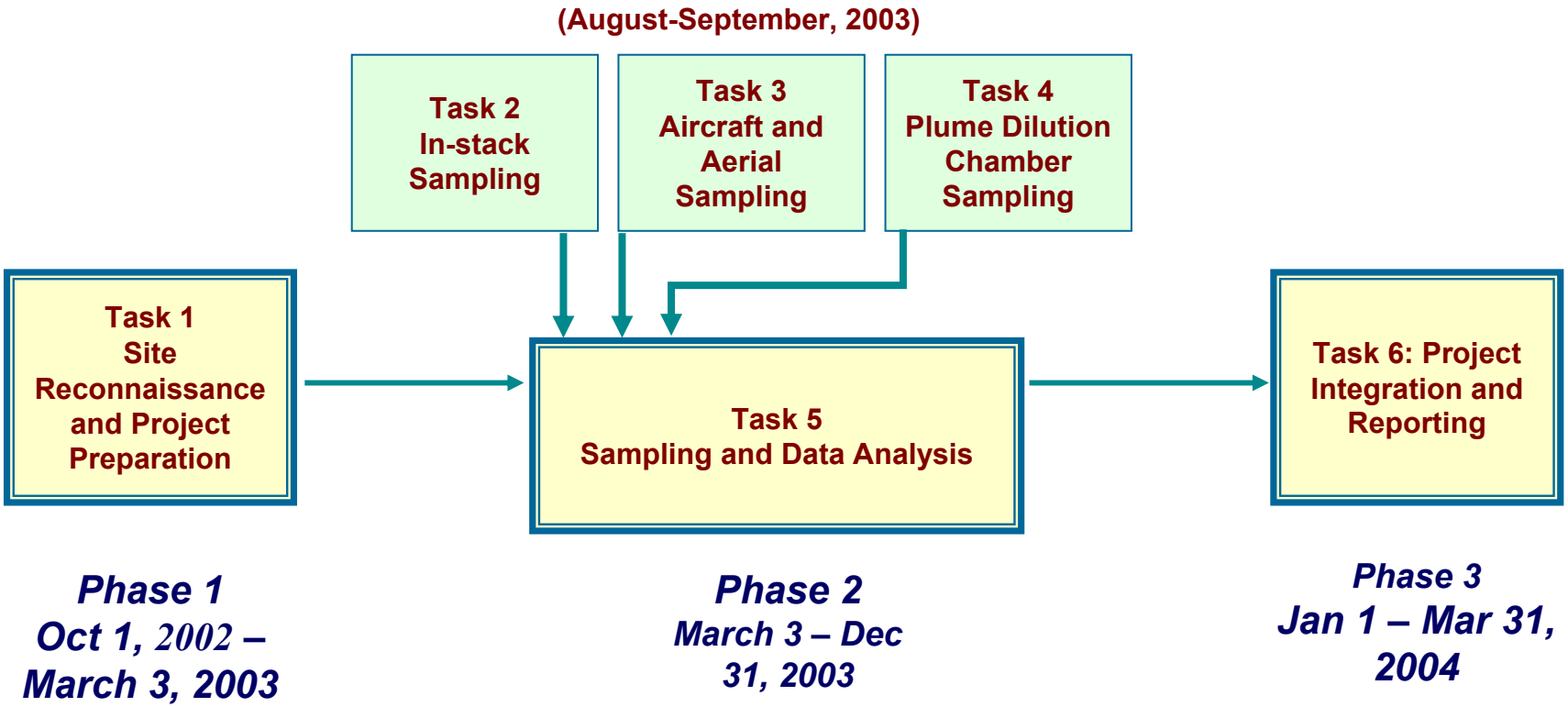
PROJECT SCHEDULE FOR PLEASANT PRAIRIE EXPERIMENT



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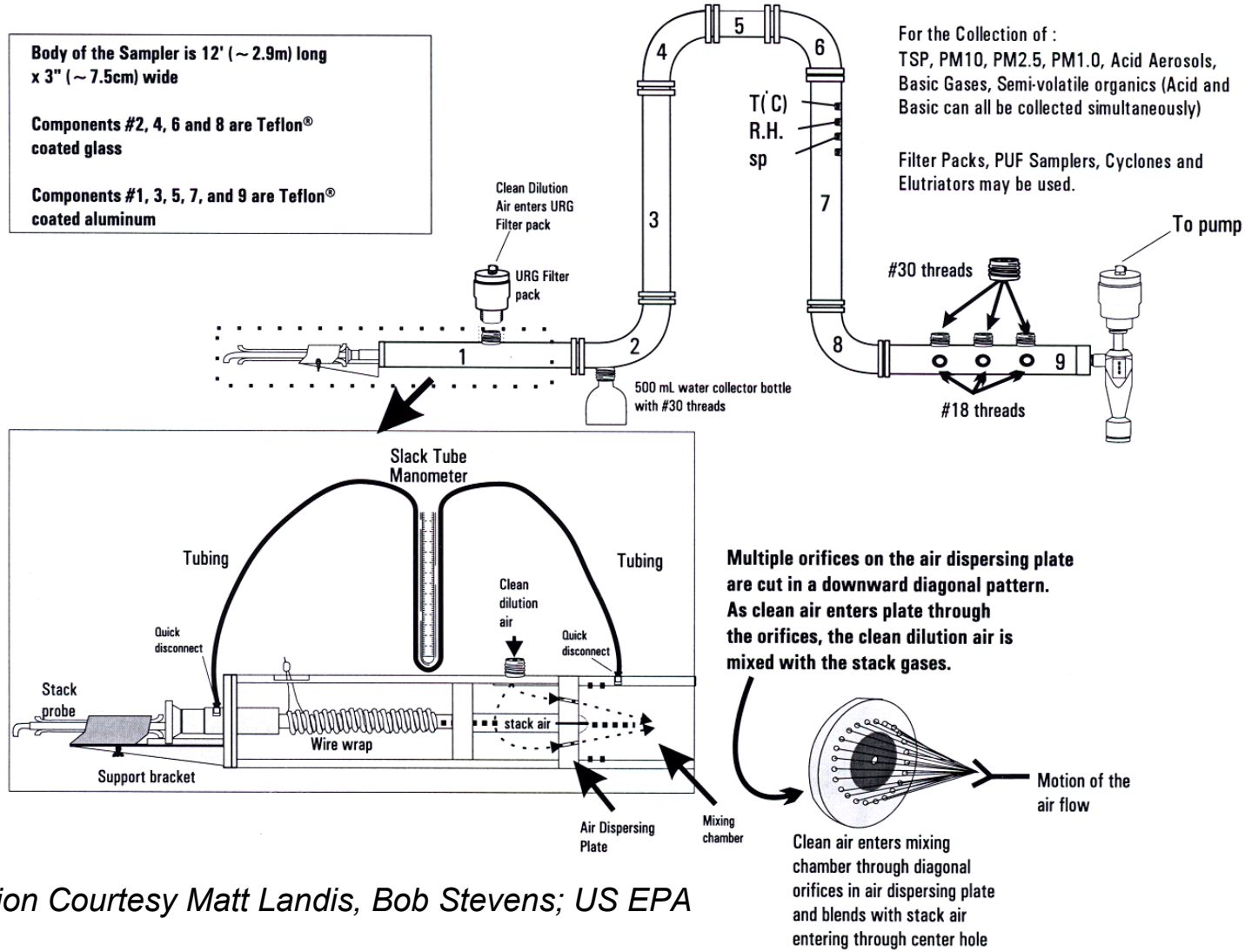
Dynamic Plume Dilution Stream



Instrumentation Courtesy Matt Landis, Bob Stevens; US EPA

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HINT OF A MECHANISM????

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Yusuf et al., 2003

- "Homogeneous and heterogeneous reactions of atmospheric mercury(II) with sulfur(IV)," Huda Yusuf, Nazafarin Lahoutifard, Kirsty Maunder, and Susannah L. Scott (presented at: XII International Conference on Heavy Metals in the Environment", Grenoble, France, May 26-30, 2003)
  - *Abstract*. Atmospheric models suggest that the reduction of Hg(II) to Hg(0) by S(IV) prolongs the residence time of mercury. The redox reaction was investigated both in the aqueous phase (where the reductant is sulfite) and on particulate matter (where the reductant in $SO_2(g)$). In both cases, one of the ultimate products is HgS. A mechanism is proposed involving formation of Hg(0) followed by mercury-induced disproportionation of SO_2 *[for SO_2 ~ Hg]*
- Proposes $HgO(s) + SO_2(g) \rightarrow Hg(0)(g) + SO_3(g)$ for SO_2 >> Hg

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RESEARCH TEAM

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Research team, EPRI program on mercury reactions in power plant plumes

- ARA
- Atmospheric and Environmental Research, Inc.
- Energy & Environmental Research Ctr, University of North Dakota
- Frontier Geosciences
- National Energy Technology Laboratory, U.S. DOE
- State of Florida
- State of Wisconsin Department of Natural Resources
- State of Wisconsin Division of Energy
- Southern Company
- Tennessee Valley Authority
- U.S. Environmental Protection Agency
- University of Alabama at Huntsville
- University of North Dakota
- We Energies
- Wisconsin Focus on Energy
- Many others: Allegheny Power, American Electric Power, Constellation Energy, Detroit Edison, Duke Energy, MEAG, Oglethorpe Power, TXU

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Global inventory (1995 datum)

Pacyna et al., "Mapping 1995 global anthropogenic emissions of mercury," *Atmosph. Env.*, 2003

Global emissions of total mercury from major anthropogenic sources in 1995 (in tonnes)

Continent	Stationary combustion	Non-ferrous metal production	Pig iron and steel production	Cement production	Waste disposal	Total
Europe	185.5	15.4	10.2	26.2	12.4	249.7
Africa	197.0	7.9	0.5	5.2		210.6
Asia	860.4	87.4	12.1	81.8	32.6	1074.3
North America	104.8	25.1	4.6	12.9	66.1	213.5
South America	26.9	25.4	1.4	5.5		59.2
Australia & Oceania	99.9	4.4	0.3	0.8	0.1	105.5
Total	1474.5	165.6	29.1	132.4	111.2	1912.8[a]

[a] In addition, emission of about 514 tonnes of Hg was estimated for chlor-alkali plants, gold production, and the use of mercury for various purposes (primary battery production, production of measuring and control instruments, production of electrical lighting, wiring devices, and electrical switches) in 1995.

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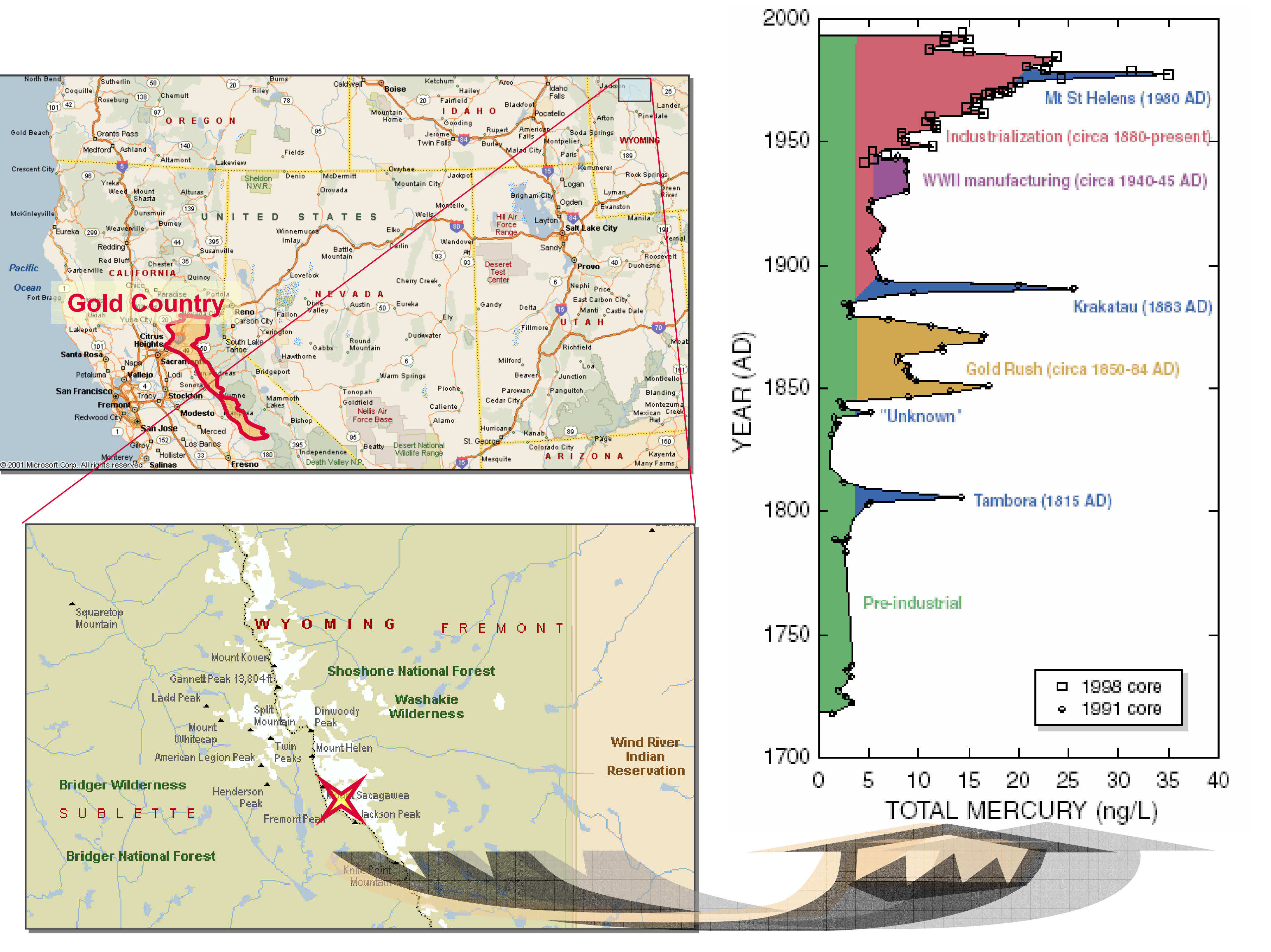

Gold Country
O R E G O N
I D A H O
WYOMING
U N I T E D S T A T E S
N E V A D A
U T A H
CALIFORNIA
A R I Z O N A
Pacific
Ocean
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W Y O M I N G
F R E M O N T
S U B L E T T E
Shoshone National Forest
Washakie Wilderness
Bridger Wilderness
Bridger National Forest
Wind River Indian Reservation
Squaretop Mountain
Mount Koven
Gannett Peak 13,804 ft
Ladd Peak
Split Mountain
Dinwoody Peak
Mount Whitecap
Twin Peaks
Mount Helen
American Legion Peak
Henderson Peak
Sacagawea
Fremont Peak
Jackson Peak
Knife Point Mountain
YEAR (AD)
TOTAL MERCURY (ng/L)
Mt St Helens (1980 AD)
Industrialization (circa 1880-present)
WWII manufacturing (circa 1940-45 AD)
Krakatau (1883 AD)
Gold Rush (circa 1850-84 AD)
"Unknown"
Tambora (1815 AD)
Pre-industrial
1998 core
1991 core